Gradient Techniques For Nanotechnology Development

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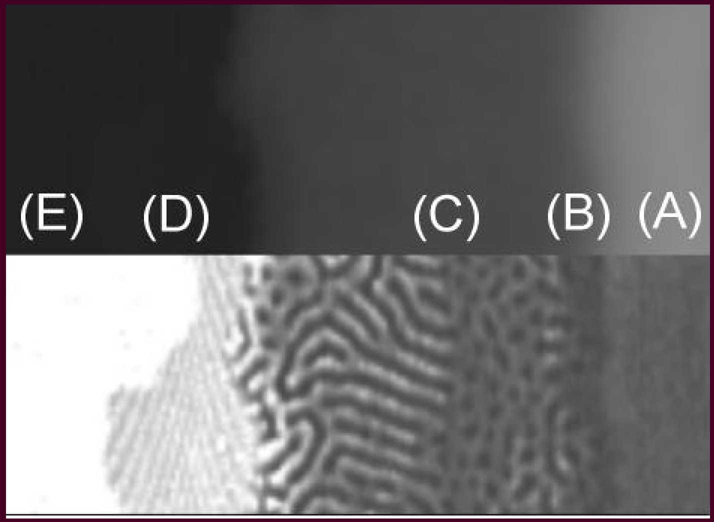
An “impromptu” gradient experiment

Thin film morphology of PS-PLMA block copolymer

M.J. Fasolka and A.M. Mayes et al, Macromolecules **33** 5702 (2000)

AFM height

AFM phase



- AFM of droplet edge
- Morphology/thickness relationships

Advantages:

- Illuminates morphology/thickness relationship *in a single micrograph*
- Single high-info specimen with uniform processing

Drawbacks:

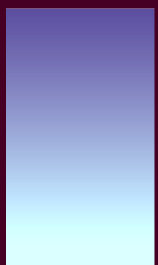
- Generally *Qualitative*
- Limited specimen scope
  - steep gradient
- Hard to reproduce

Building Better Gradient Techniques

NIST
Combinatorial
Methods Center
www.nist.gov/combi

- Combi and high-throughput methods for *Materials Research*
- 21 Member industrial consortium
- Education and Outreach

Continuous Gradient Specimens



- Gradual and steady change in a property as a function of distance

NCMC Gradient Specimens

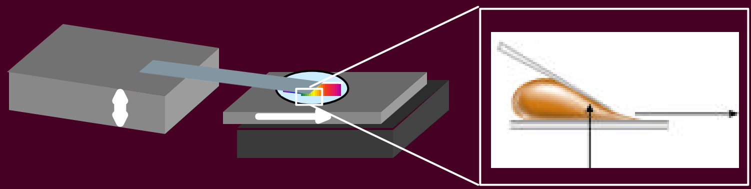
- Properties of interest to materials researchers
- Tailored gradient scope and steepness
- Reproducible fabrication

Crossed-Gradient Combinatorial Libraries

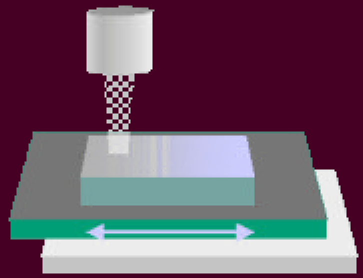
- Orthogonal arrangement of 2 gradient specimens
- Includes every combination of 2 variables within scope of gradients

NCMC Gradient Toolbox

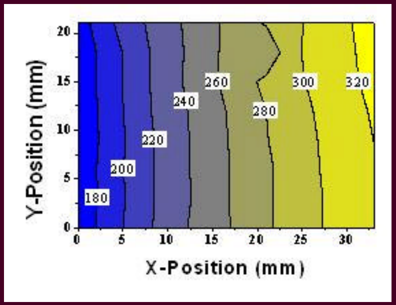
Polymer Film Thickness Gradient (C. Meredith)



NIST Gradient Flow Coater for dilute polymer solutions

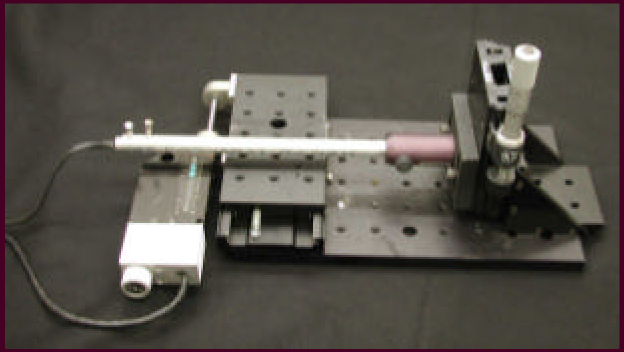


Automated Spot Interferometer

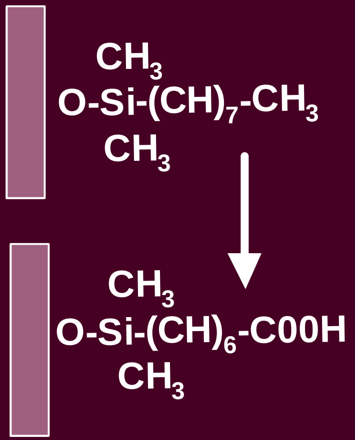


Gradient Range:
20-500nm in 100 nm steps

Surface Energy Gradient (A. Sehgal, A. Crosby, M. Fasolka)

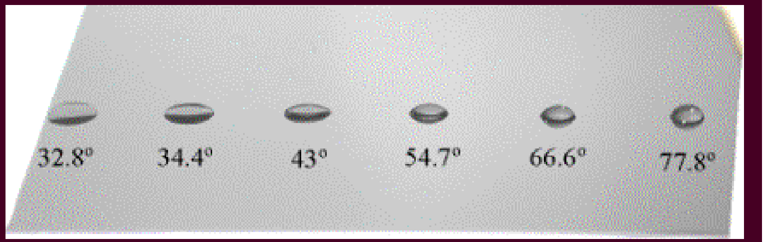


UV-ozone Exposure Gradient Device



Exposure dependent SAM conversion

Automated contact ∠ measurements

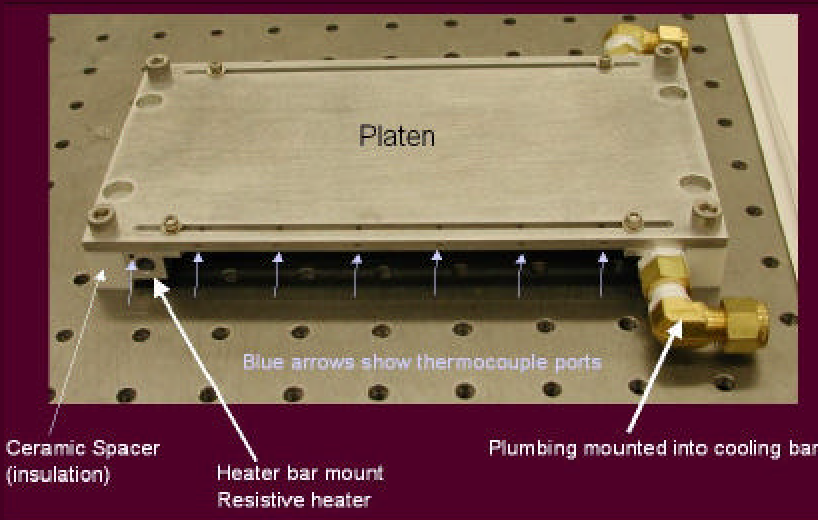


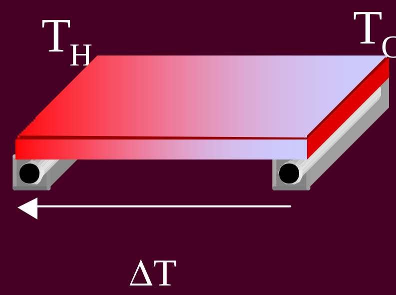
Gradient Range:
20-78 mJ/m²
Continuous or step-like

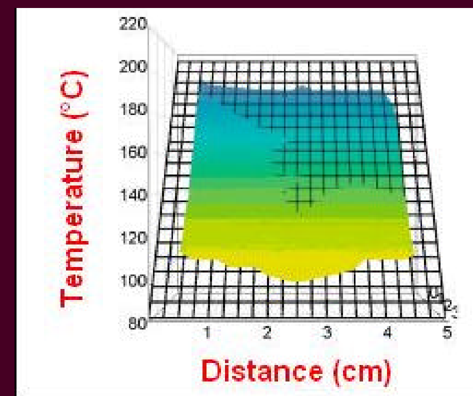
NCMC Gradient Toolbox

Temperature Gradient (K. Beers, C. Stafford)

Gradient Hot-stage







Gradient Range:
20 ºC to 250 ºC in 100 ºC steps

Other Gradients and Gradients in Development

- Composition Gradients (Polymers, Additives from Dilute Solution)
- Surface Texture Gradients (Patterned and Random Roughness)
- Cross-linking Gradients

Gradient Applications in Nanotechnology

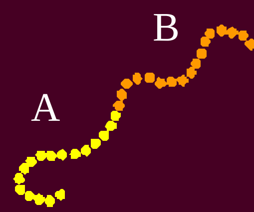
Examples from NCMC Research

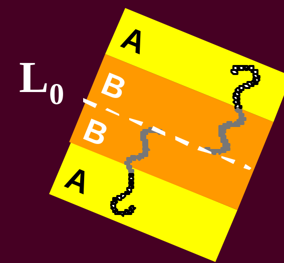
- Thorough Behavior Mapping
  Ultra-high information density specimens
- Process or Parameter Optimization
  Precise determination of best conditions
- Advancement of Nano-scale Measurements
  Reference Substrates for Advanced SPM Techniques

Block Copolymer (BC) Thin Film Basics

Review: M.J. Fasolka & A.M. Mayes, Annu. Rev. Mat. Sci. 31, 323 (2001)

- Nanometric self assembly
  - L_0=10nm - 100nm
- Surface Directed Morphology

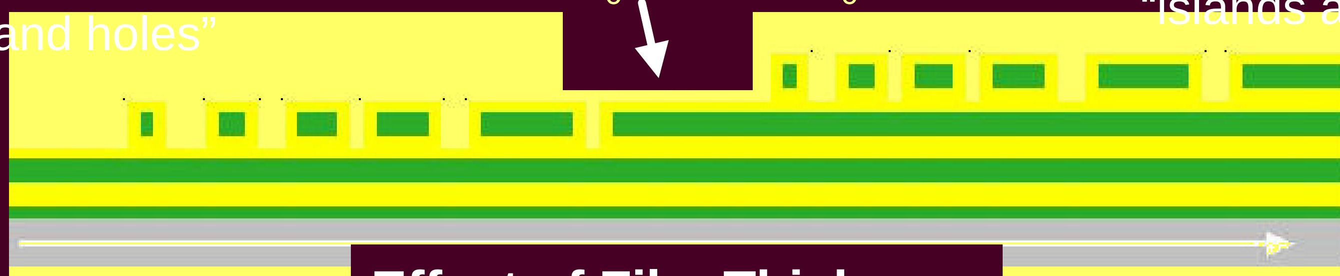




Surface structure:
“islands and holes”

Smooth film:
$h = nL_0, (m+1/2)L_0$

Surface structure:
“islands and holes”

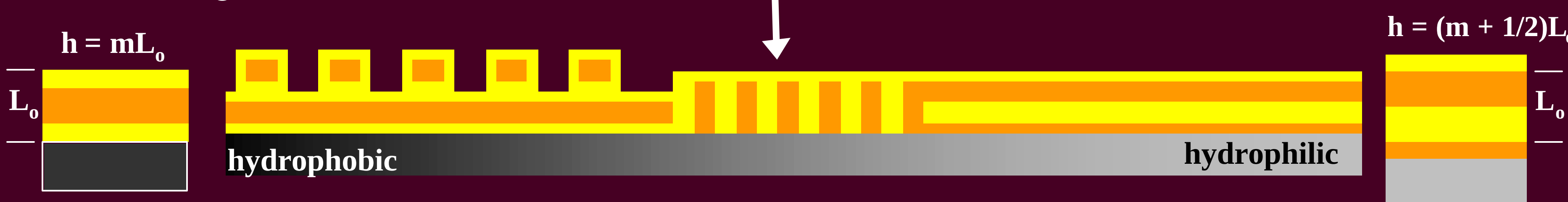


Effect of Film Thickness

Symmetric wetting

Neutral surface:
perpendicular domains

Anti-Symmetric wetting

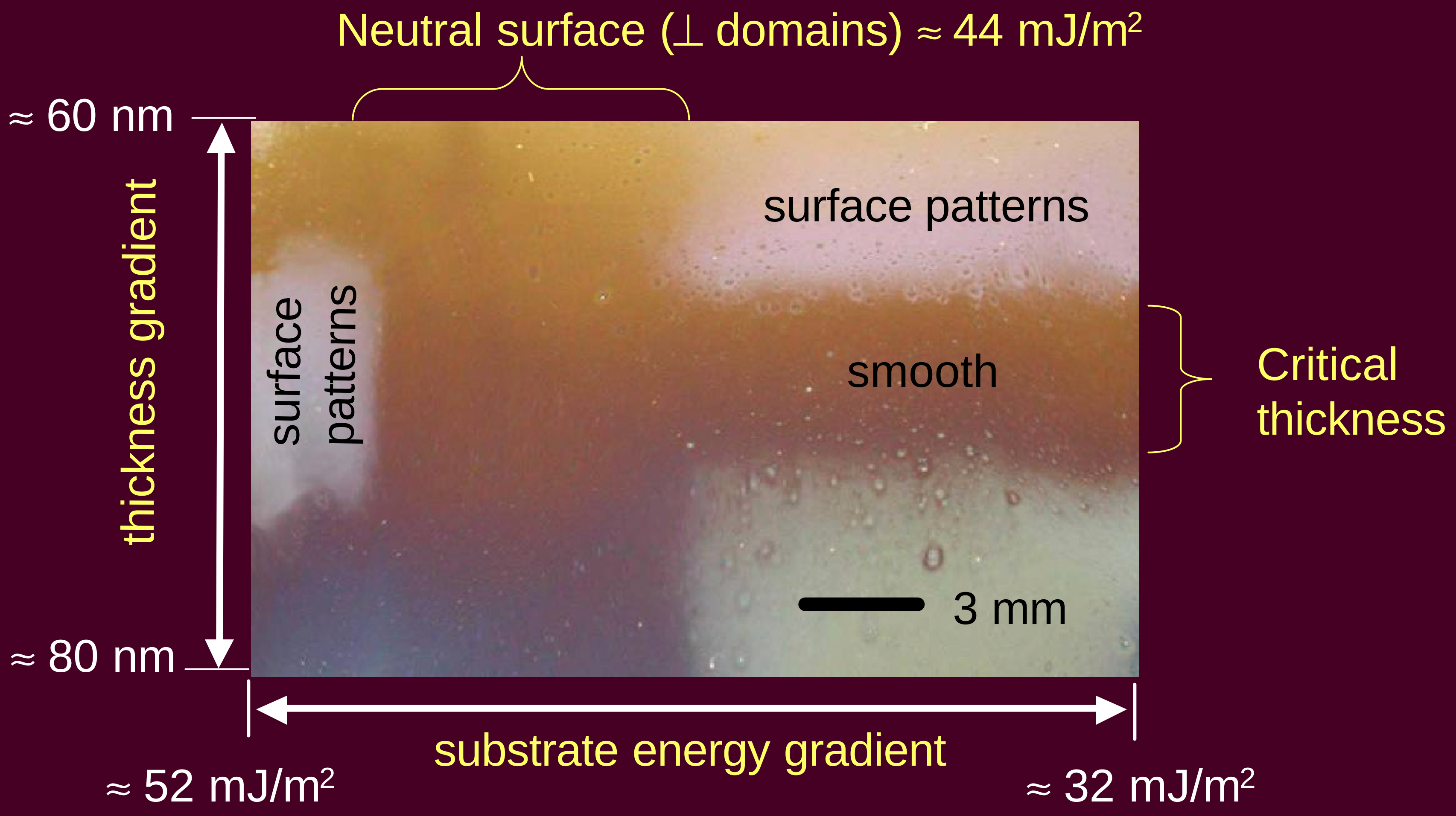


Effect of Substrate Surface Energy

Mapping: BC Film Gradient Combi Library

A.P. Smith et al, Macromolecules Rapid Communications 2003; 24(1): 131
A.P. Smith et al, Physical Review Letters 2001; 8701(1): 5503

Polystyrene-b-Polymethylmethacryate film (After T.P. Russell)



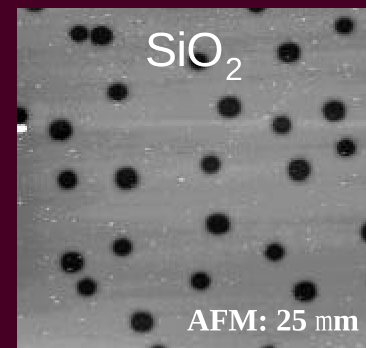
Optimization: BC Film Gradient on Patterned Substrate

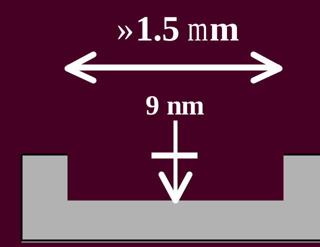
M.J. Fasolka, T.A. Germer, A. Karim, & E.J. Amis, NIST

Goals:

- Map behavior of BC Films on topographically structured substrates
- Find conditions for "anti-conformal" film on a specific substrate

Pseudo random array of pits

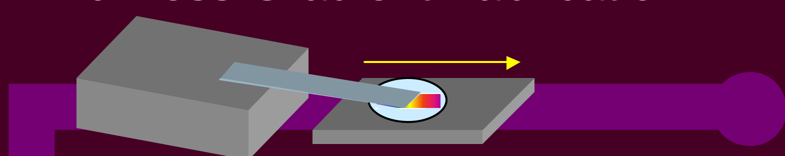




Pit profile

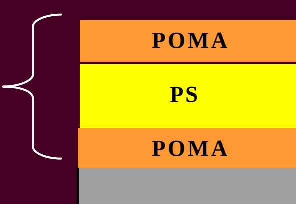
High-throughput Gradient Experiment:

Thickness Gradient Fabrication

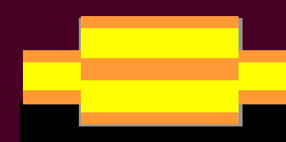


Polystyrene-b-Poly(n-octyl methacrylate)

Lamellar period L_0=23nm

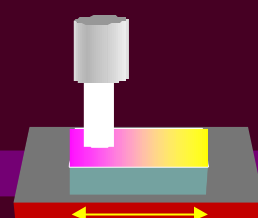


goal



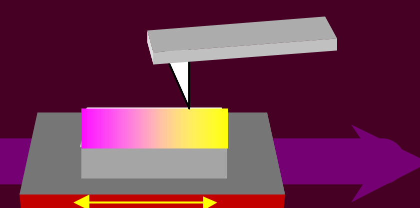
2 specimens

35+ test points



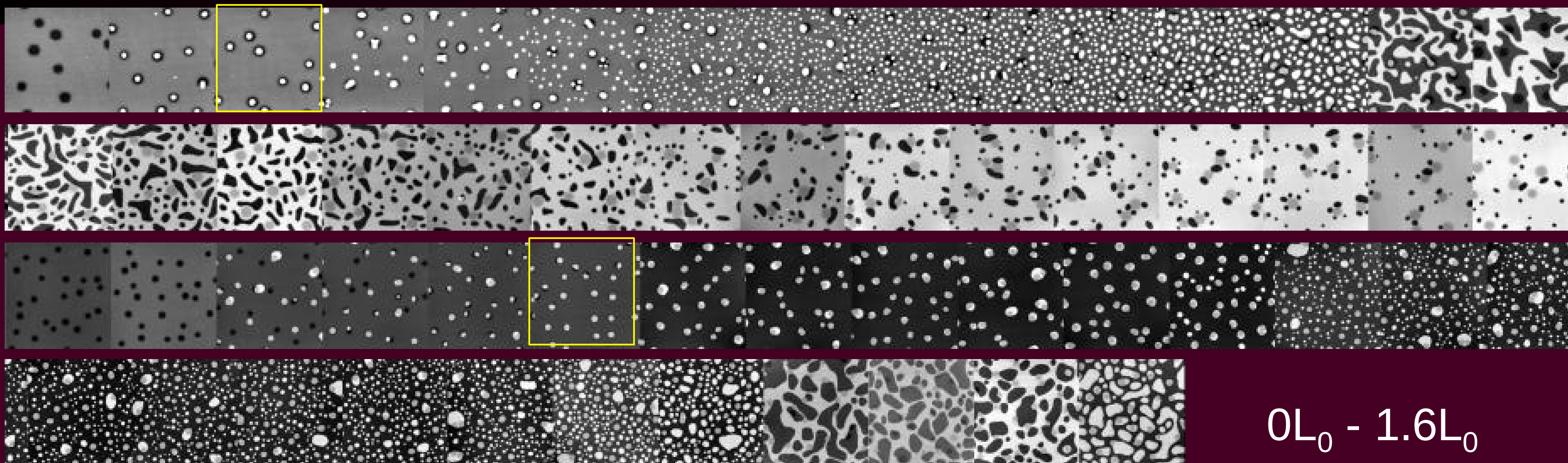
Auto Interferometry

24hr @ 180 ºC



Auto AFM

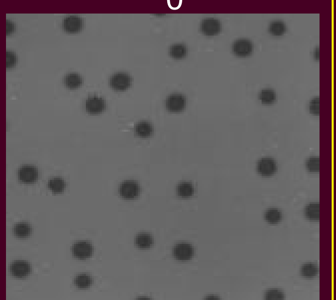
Optimization: BC Film Gradient on Patterned Substrate



$0L_0$ - $1.6L_0$

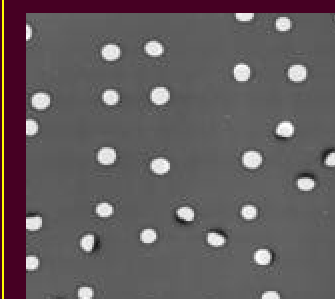
Rich thickness-dependent behavior:

L_0



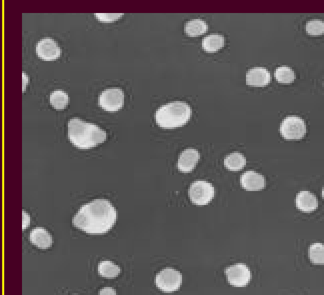
Conformal

$1.15L_0$



Anti-conformal

$1.2L_0$

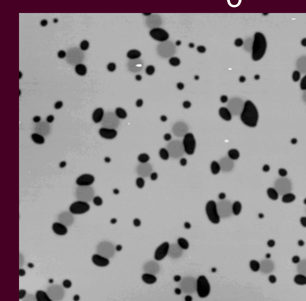


Anti-conformal
+
Non-conformal

$1.6L_0$

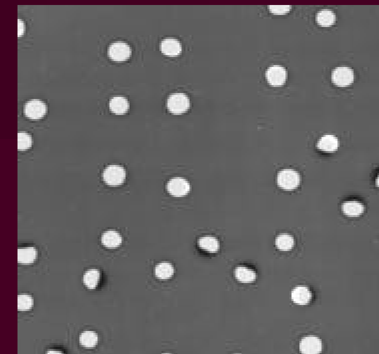
Non-conformal
+
Conformal

$0.94\ L_0$



Hole clustering

BC Film on Patterned Substrate



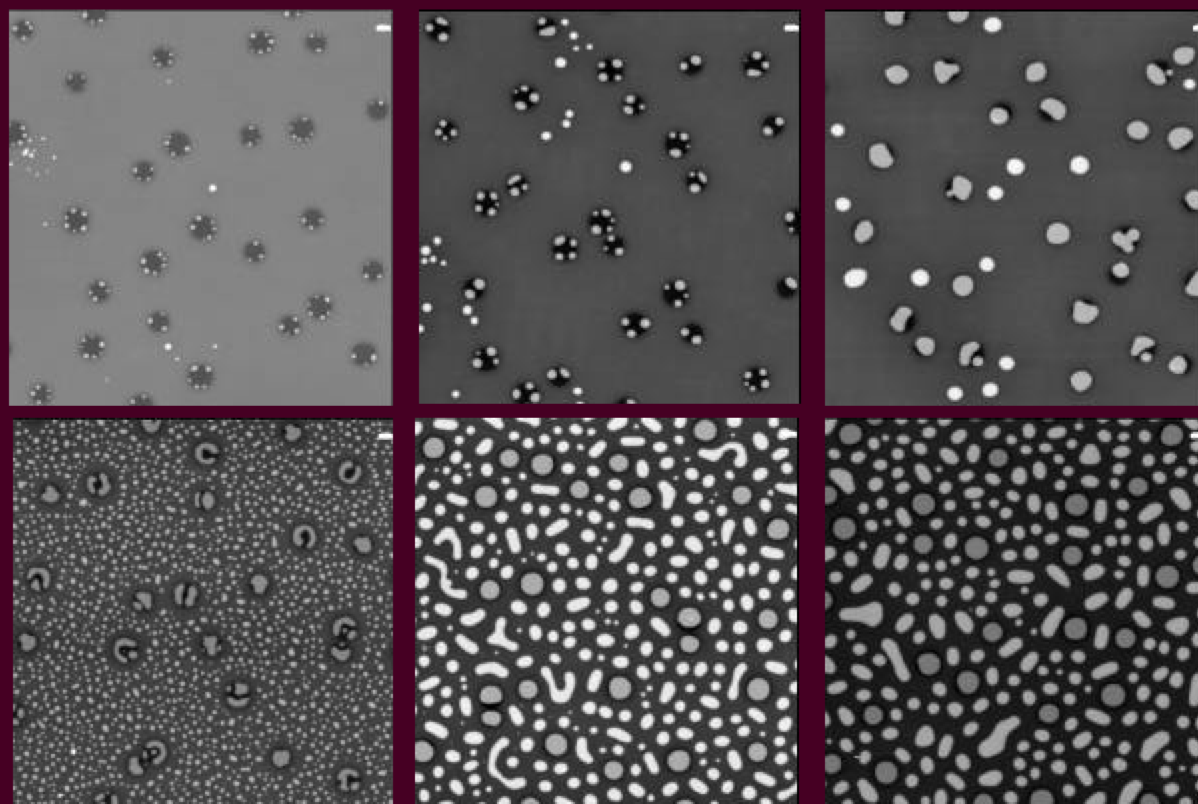
When and Why do anti-conformal films occur?

- Island area equals pit area (15% pit area $\Rightarrow$ $0.15nL_0$)
- Pits nucleate islands

1 min | 5 min | 20 min

$0.2L_O$

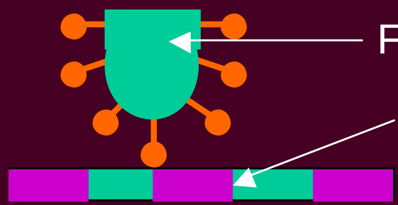
$0.4L_O$



Measurements: Gradient Reference Substrate for CFM

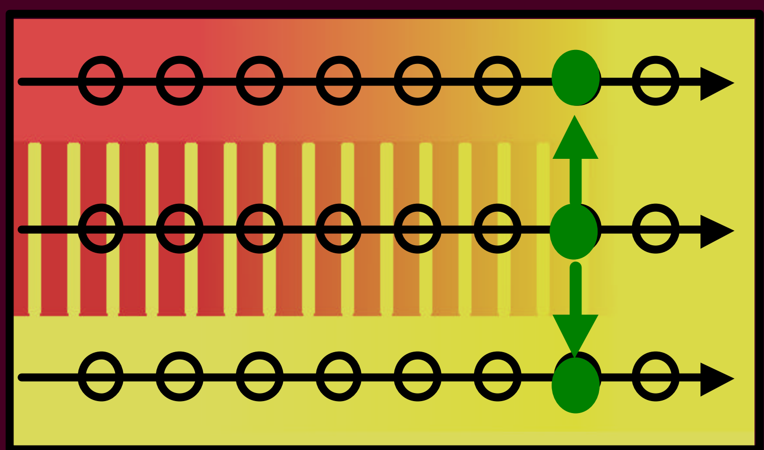
M.J. Fasolka, T. Nguyen, A. Karim, K. Briggman, NIST

Advance *Chemical Force Microscopy* as a quantitative measurement technique



Reference Specimens that:

- Calibrate image contrast
- Challenge sensitivity



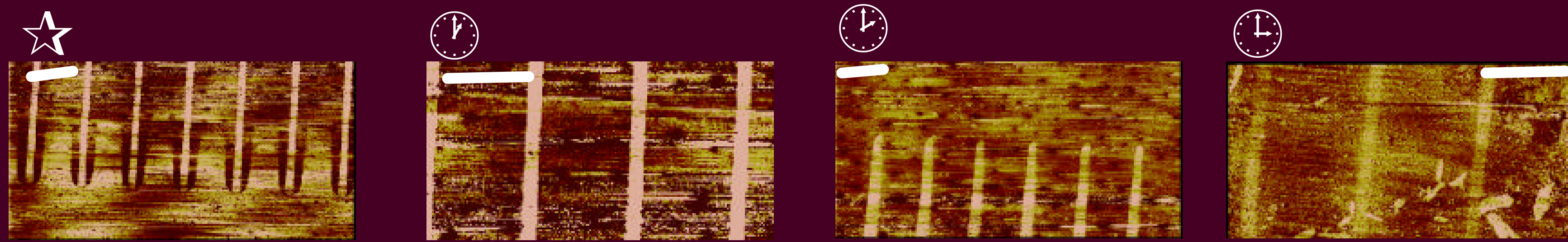
- Chemical contrast gradient
- Relates contrast to traditional analysis
- Gauges sensitivity

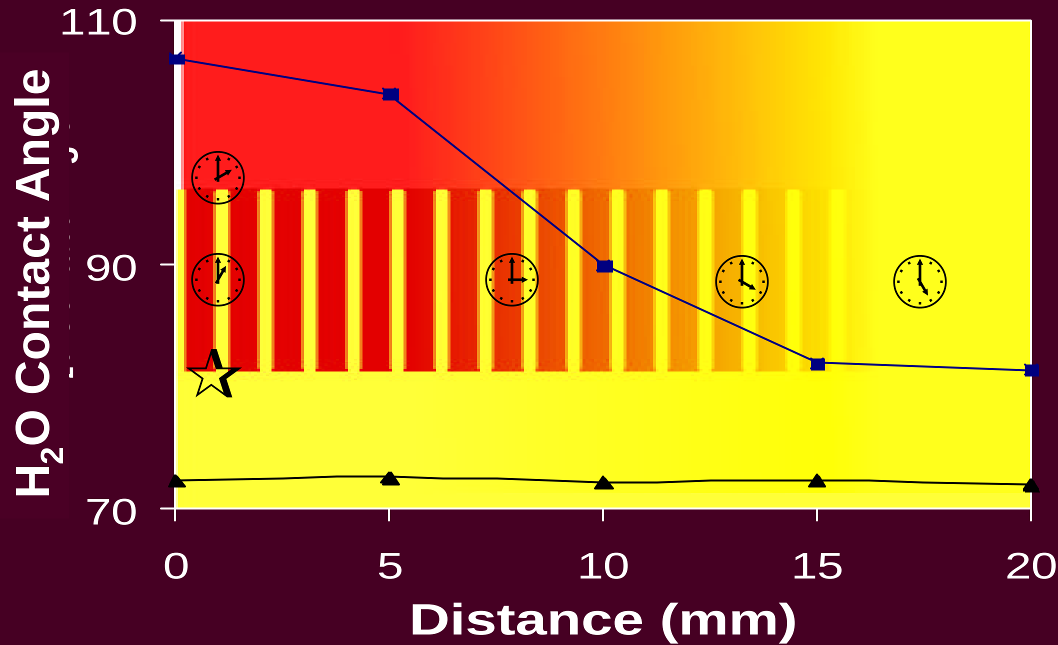
<u>Fabrication and Calibration of Specimen</u>

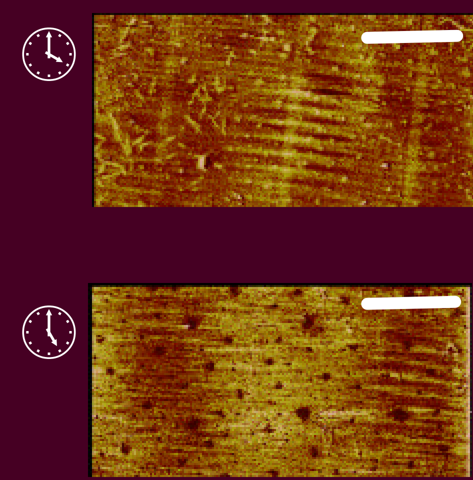
- Hydrophilic and Hydrophobic SAMs printed with PDMS stamp
- *Gradient in UV exposure* gradually converts hydrophobic SAM to hydrophilic species.
- Contact ∠ measurements calibrate contrast in the patterned area.

Measurements: Gradient Reference Substrate for CFM

Contact-Mode Friction AFM Images







Scale bars are 10mm
Images have equal z-scales

Print: $(CH_2)_{17}$-CH_3 Thiol SAM
Fill: $(CH_2)_{15}$-COOH Thiol SAM

Linear UV Exposure Ramp: 0 - 60s

Summary: Gradients for Nanotechnology

NIST Combinatorial Methods Center Capabilities:

- Purpose and Scope
- Gradient Tool Box Examples
  - Thickness
  - Surface Energy
  - Temperature and others

Utility of Gradients for Nanotechnology Development

- Thorough Behavior Mapping
  Ultra-high information density BC Film Library

- Process or Parameter Optimization
  Determination of conditions for anti-conformal films

- Advancement of Nano-scale Measurements
  Reference Substrates for Chemical Force Microscopy

Contributors

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Kimberly Briggman (Optical Technology Division)
Tihn Nguyen (Building and Fire Research)

Advertisements: *(ask for a CD)*

Interested in Combinatorial and High-Throughput Materials Research?

Post-doctoral Positions are Available!

- **Combi and HTE for Polymers and Nanotechnology**
- **Excellent opportunities for industrial interaction**

Contact: Michael Fasolka at mfasolka@nist.gov

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NCMC Member Consortium: